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Final Technical Report
(November 15, 1961)
SOLID STATE PROPERTIES
OF NON-CONDUCTING
MATERIALS OF SIMPLE MONATOMIC
AND DIATOMIC SPECIES

by

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for

EUROPEAN RESEARCH OFFICE (9851 DU)

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ABSTRACT

During the first year of research under the above contract the problem of the stability of crystal structures for the heavy rare gas atoms has been analyzed. It is known from good experimental evidence that neon, argon, krypton and xenon crystallize in the face-centered cubic structure (fcc), whereas helium under pressure crystallizes in the hexagonal close-packed form (hcp). According to calculations based on twobody forces, however, the hexagonal lattice should be somewhat more stable for all solids involved.

The underlying hypothesis for the analysis has been that the cubic structure becomes more stable if deviations from the assumption of twobody forces are taken into account. Since, in principle, there occur many possible types of such manybody interactions, a systematic analysis of these various effects was first undertaken, based on a cluster expansion and making use of a perturbation treatment.

Simultaneously, a number of pilot calculations was carried out, with the aim of acquiring better insight in the different characteristics of the various possible manybody effects. From the analysis of spectra from trapped free radicals in molecular crystals it had been found that an argon matrix behaves to some extent like a nitrogen matrix. To provide a basis for the explanation of this curious phenomenon, it was shown that the crystal field in solid argon is not simply the sum of fields from separate atoms, but that deviations occur in the form of higher multipole moments induced by electron exchange between neighboring atoms. Such exchange effects imply, for example, that there is a quadrupole contribution arising from an argon-diatomic "molecule", to the crystal field. It was found that such a quadrupole moment is not small compared to that of a nitrogen molecule and that it may, at least in part, account for the splitting of spectral lines emitted by excited free radicals (nitrogen atoms) in an argon matrix.

Also, preliminary calculations were performed with various forms for the threebody force (different angular and radial functions). The differences between crystal sums for the hcp- and fcc-lattices increase in general as the forces become of shorter range, and increase as well with higher angular dependence (increasing powers of $\cos \theta$, where θ is the angle between the lines connecting any two pairs of atoms on a triangle). The relative difference between the crystal sums may be of either sign and is, for reasonable analytic threebody potentials, of the order of magnitude of ten to twenty percent.

After this stage of the research had been completed, the general treatment of threebody forces between rare gas atoms in first order of perturbation theory was initiated. To avoid difficulties associated with the use of a multipole expansion for the electrostatic interactions between the atoms (such series diverge generally for all interatomic distances), the integrals were evaluated exactly on the basis of a model calculation, in which the electron charge distribution of the atoms is approximated by a Gaussian function with an adjustable parameter. Values for this parameter can be determined empirically, both at large and at small distances between the atoms.

The analysis was restricted to triangles formed by a central atom and its twelve nearest neighbors in either lattice (fcc and hcp). It was found that the relative deviation from the additive first-order energy is negative for an equilateral triangle, amounting to about twenty percent. For a 120° -configuration this relative difference is much smaller and always positive, whereas for a linear symmetric array the effect is again large, positive, and decreasing practically linearly with interatomic distance.

A comparison, finally, between the 66 triangles, formed by a central atom and its twelve nearest neighbors in the hcp- and fcc-structures (57 are the same between the lattices, whereas 9 are different) revealed that, although this threebody effect contributes significantly to the first-order

energy of the crystals, the difference between the two structures is still too small to account for the observed stability of the face-centered cubic structure.

Therefore, a second-order calculation was started on the same basis, leading to manybody contributions to the van der Waals-forces. This analysis is at present under way.

OUTLINE OF RESEARCH PROJECT

Concerning properties of materials in general, it is nowadays recognized that no essential progress is possible without extensive fundamental research. In the past, most of the theoretical investigations in the field of properties of solid materials have been directed towards an explanation of phenomena associated with metallic substances, of semiconductors, and, to a lesser extent, of ionic crystals. Compared with this group of materials, the theory of molecular solids (insulators) has received but little attention, and even the most striking facts exhibited by such materials often lack a satisfactory explanation. It has become more and more urgent to try to fill this gap, since molecular solids have become of increasing importance also from a practical point of view. As an example it might be mentioned that the stability of the close-packed cubic crystal structure of the heavy rare gases (neon, argon, krypton and xenon) cannot be explained on the basis of existing theories. One finds that the hexagonal close-packed crystal form (the helium structure) should be more stable than the cubic structure, and this result is remarkably insensitive with respect to the precise form of intermolecular potentials. Concerning this problem the present investigator has suggested that an explanation may be found on the basis of the effect of manybody forces of the van der Waals-type (second order of perturbation theory) on the stabi-

lity. Preliminary calculations have shown that this explanation may be the correct one, and that present theories of molecular solids need considerable modification.

The crystals of nitrogen and carbon monoxide are also cubic close-packed at the lowest temperatures, but show a transition to the hexagonal closest packing at 35° K and 61° K, respectively. The present investigator has suggested that the stability of these crystals and the transition mechanism may involve orientational interactions (e. g. those due to permanent electric quadrupole moments) in the solids. The cubic structure is favored by quadrupole interactions in the solids, whereas the hexagonal structure is preferred by anisotropic components of the van der Waals forces. As the temperature increases and herewith the rotational amplitudes of the molecular axes, the quadrupole forces, being of first order, die out much more quickly than the (second-order) van der Waals forces. The results obtained so far suggest strongly that this explanation may be the correct one, although a quantitative theory is still lacking.

Molecular solids have recently become of importance also as materials in which free radicals can be trapped and stored. The results obtained in this field provide an invaluable experimental background for the development of a crystal field theory of molecular solids. This investigator has been associated with the Free Radicals Research Group at the National Bureau of Standards in Washington, D. C., and has performed some preliminary calculations which seem to indicate that present theories of molecular solids are in need of substantial improvement in order to yield satisfactory agreement with experimental data.

SUMMARY OF RESULTS OBTAINED DURING FIRST YEAR

The results obtained so far may be divided into four different categories :

I. Development of a general theoretical method to classify all possible types of manybody interactions in molecular solids. This analysis is based on the method of Localized Orbitals in Crystals. It leads to a double series expansion for arbitrary properties of molecular crystals : one, in terms of linked exchange-clusters of increasing size, and one, in terms of increasing orders of perturbation theory. (Special Technical and Scientific Reports No. 1 and 2, January 30 and July 31, 1961.)

II. Evaluation of the triatomic, first-order manybody effect. The calculation makes use of a Gaussian effective-electron model for rare gas atoms (Special Technical and Scientific Report No. 2, July 31, 1961).

III. Application to the stability of crystal structures of the heavy rare gas atoms, for a central atom and its twelve nearest neighbors. The hexagonal close-packed and face-centered cubic lattices are compared.

IV. Application to the crystal field in molecular solids, in connection with a future analysis of spectra emitted by free radicals trapped in solid argon. The exchange quadrupole moment for two argon atoms in solid argon is calculated (Special Technical and Scientific Report No. 2, July 31, 1961).

The analysis of threebody interactions in second order of perturbation theory, again based on a Gaussian model, is at present under way. A Special Technical and Scientific Report No 4 (August 15, 1961) was issued, containing details and further technical information concerning the calculations for I and II.

ANALYSIS OF RESEARCH PERFORMED

A. GENERAL

The following sections contain a detailed discussion of results obtained on the problem of stability of crystals of the heavy rare gas atoms. Excluded from the considerations is solid helium, since this element crystallizes at moderate pressures in a hexagonal close-packed lattice, which result is predicted even by a simple analysis based on pair-interactions between the atoms in the crystal. This result is not changed by any manybody effect of the type to be discussed below, since such effects depend essentially on the amount of overlap between neighboring atoms in the solid. Due to the small size of the helium atom, and its large zero-point energy which results in a relatively large nearest neighbor distance, overlap effects are entirely negligible in this case.

The analysis of manybody interactions in molecular solids will be based on the method of Localized Orbitals in Crystals (also called the Crystal Valence Bond method, the crystal analogon of the Heitler-London method for molecules). We could, of course, just as well have used a Crystal Orbital method (the crystal analogon of the Molecular Orbital method for molecules, also called the LCAO-, or Bloch-scheme, or the Tight-Binding Approximation) which gives results identical with those of the Localized Orbitals in the case of closed shells of electrons, as with the rare gas atoms.

Further, we are considering crystals which are held together by relatively weak forces of the van der Waals-type. These interactions are very much weaker than those involved in chemical binding, or in ionic crystals, or even compared with the cohesive energies of metals. In good approximation, the physical properties of these systems may then be described by means of perturbation methods.

It will be shown below that any property of the crystal (in particular, the static lattice energy) can be expressed in terms of a double series expansion : one, in terms of contributions due to linked exchange-clusters of increasing size, and one, in increasing orders of perturbation theory. Molecular crystals may thus be defined by the requirement that this double series expansion converges rapidly in both respects.

B. SYSTEMATIC ANALYSIS OF MANYBODY INTERACTIONS IN MOLECULAR SOLIDS

An analysis is undertaken of the different possible types of simultaneous interactions between more than two atoms or molecules in so-called molecular solids. The analysis is carried out on the basis of a double series expansion : 1) in terms of linked exchange-clusters of increasing numbers of atoms; 2) as a series in increasing orders of perturbation theory. The use of a multipole series for the electrostatic interactions between different atoms is avoided by retaining this interaction in unexpanded form. Instead, an effective-electron model is used with a Gaussian form for the charge distributions. The method is illustrated by computing the exchange quadrupole moment of two argon atoms as a function of their distance. Calculations by P. Rosen and by Shostak for first-order interactions between three helium atoms are extended to atoms of the heavy rare gases. It is found that the relative magnitude of this manybody effect may amount to twenty percent of the first-order interaction energy. Possible implications with respect to stability of the cubic structures of heavy rare gas crystals are briefly discussed.

INTRODUCTION

The possible importance of simultaneous interactions between more than two atoms, molecules or nucleons for the interpretation of properties of compressed gases, liquids, solids and nuclear matter has from time to time aroused interest in the literature. In molecular physics, this interest arose principally from a possible rôle of manybody interactions in a solution to the problem concerning the stability of the observed cubic crystal structures of the heavy rare gases. Calculations based on pair-interactions had revealed that a hexagonal structure should be somewhat more favorable, in contradiction with experiment. It seemed, therefore, that the pair-assumption (additivity) of interactions between rare gas atoms could not be reconciled with their crystal structure.

In contrast with nuclear problems we possess for molecular systems complete knowledge regarding the origin of the forces between the particles, so that, in principle, it should be possible to assess the significance of manybody interactions for the properties of molecular solids, for example. Yet, the explicit calculations which have so far been carried out were either based on approximations which clearly ceased to be satisfactory at relatively small interatomic distances, or they concerned systems of little interest.

As an example of the first category, we mention the so-called triple-dipole effect for three rare gas atoms, evaluated by Axilrod and Teller ¹, and Axilrod ². This calculation concerns the induced-dipole interaction in third order of perturbation theory between three non-overlapping distributions of charge. As such, it constitutes simply

1. B. M. Axilrod and E. Teller, J. Chem. Phys. 11, 299 (1943)

2. B. M. Axilrod, J. Chem. Phys. 17, 1349 (1949); 19, 719, 724 (1951)

an extension of van der Waals-interactions, as calculated by London, to third order. But manybody interactions occur already in lower orders of perturbation theory (induced by electron exchange); in addition, the use of a multipole expansion for the electrostatic interactions becomes increasingly less accurate as the distances between the atoms decrease. In fact, such series usually do not converge at all^{3, 4, 5}. Tredgold and Ayres⁶ have modified this calculation by using a Gaussian distribution function for the negative charge cloud of each atom, and treating the overlap of charge distributions of neighbouring atoms in a classical way. This adds still another source of error, since at small distances the interactions are mainly of exchange type.

The same type of third-order effect was evaluated independently by Muto⁷ using an oscillator model for the atoms, and later extended by Midzuno and Kihara⁸. Bade⁹ computed the dipole-dipole part of the London-van der Waals interaction energy in the general order of perturbation theory, without exchange, using a model which represents each molecule as an isotropic harmonic oscillator. His results were applied to a linear chain of atoms by Bade and Kirkwood¹⁰.

On the other hand, first-order forces (exchange, chemical or valence forces) are predominant when the interatomic distances are small. Margenau¹¹ had already pointed out that they are of a manybody

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3. F.C. Brooks, Phys. Rev. 86, 92 (1952)
 4. A. Dalgarno and J.T. Lewis, Proc. Roy. Soc. (London) A69, 57 (1956)
 5. L. Jansen, Physica 23, 599 (1957); Phys. Rev. 110, 661 (1958)
 6. R.U. Ayres and R.H. Tredgold, Phys. Rev. 100, 1257 (1955); Bull. Ams. Phys. Soc. 1, Ser. II, 292 (1956)
 7. Y. Muto, Proc. Phys.-Math. Soc. Japan, 17 629 (1943)
 8. Y. Midzuno and T. Kihara, J. Phys. Soc. Japan 11, 1045 (1956)
 9. W.L. Bade, J. Chem. Phys. 27, 1280 (1957)
 10. W.L. Bade and J.G. Kirkwood, J. Chem. Phys. 27, 1084 (1957)
 11. H. Margenau, Rev. Mod. Phys. 11, 1 (1939).

type. Such an effect was evaluated for an equilateral triangle, and a linear symmetric array, of three helium atoms by P. Rosen¹², Shostak¹³ repeated the calculations for the linear array, using molecular orbitals. Unfortunately, helium is of no direct interest as far as its crystal structure is concerned, since this element crystallizes in a hexagonal lattice, in agreement with the result of calculations based on the assumption of pair-interactions.

It is, nonetheless, of interest to note the sign of the relative threebody interaction energy : both in the third-order (Axilrod-Teller) and the first-order (Rosen-Shostak) effects this sign is minus for an equilateral triangle, and plus for a linear array of atoms. This means that for an equilateral triangle the attraction, respectively repulsion is weakened compared to a simple sum over three isolated pairs, whereas the interactions for the linear array are stronger than the pair-assumption indicates.

If exchange effects are taken into account, then manybody interactions occur also in second order of perturbation theory, i. e., in the same order as the van der Waals forces^{14, 15}. In this case we have to do with a triplet of atoms, two of which overlap, whereas exchange with the third atom is not considered. Calculations were carried out on the basis of a Gaussian model for the electron charge distributions of the atoms, for the dipole-dipole and dipole-quadrupole components of the interactions. Again, the use of a multipole series renders the results unreliable for small interatomic separations, so that quantitative conclusions regarding crystal stability cannot be drawn.

12. P. Rosen, J. Chem. Phys. 21, 1007 (1953)

13. A. Shostak, J. Chem. Phys. 23, 1808 (1955); see also P.O. Löwdin, J. Chem. Phys. 19, 1570, 1579 (1951) (ionic crystal)

14. R. T. McGinnies and L. Jansen, Phys. Rev. 101, 1301 (1956)

15. L. Jansen and R. T. McGinnies, Phys. Rev. 104, 961 (1956); R. T. McGinnies, Ph. D. Thesis, Univ. of Maryland (1957).

For completeness, we mention manybody interactions between atoms or molecules which are originally in excited electron states. They are of importance at very high temperatures and have been discussed by Dahler and Hirschfelder¹⁶. Such effects, together with additional complications arising in case the charge distributions are not spherically symmetric^{15, 16}, will not be considered in this paper.

In view of the various shortcomings of the existing calculations, it seems useful to devise a systematic analysis of all possible types of manybody interactions, and to carry out their evaluation in a consistent manner, avoiding assumptions which invalidate their application to, especially, the stability of rare gas crystal structures. Since the interactions in molecular crystals are very weak compared to those in metals or in ionic crystals, we will use a perturbation expansion starting from free-atom wave functions, but avoid using a multipole series for the perturbation.

LINKED EXCHANGE-CLUSTER EXPANSION

Starting from ground-state free-atom wave functions $\varphi_a, \varphi_b, \varphi_c, \dots$, where a, b, c, \dots denote atoms, which are antisymmetric with respect to exchange of electrons of the same atom, we write the zeroth order wave functions, except for normalization, of the assembly of atoms as (Slater determinant)

$$\varphi^{(0)} = \sum_{\lambda} (-1)^{\lambda} P_{\lambda} \varphi_a \varphi_b \varphi_c \dots \dots \quad (1)$$

16. J. S. Dahler and J. O. Hirschfelder, J. Chem. Phys. 25, 986 (1956)

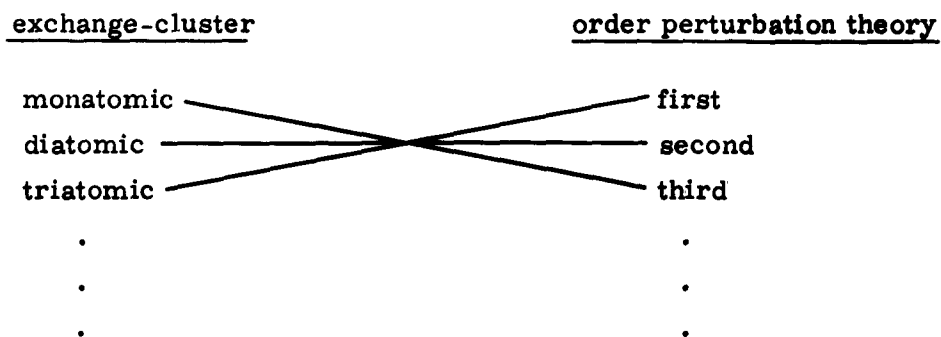
an antisymmetric sum of products of atomic wave functions; P_λ exchanges electrons between different atoms, or it denotes a combination of inter- and intra-atomic exchange.

Relative to a fixed association of electrons with the different atoms, each P_λ in (1) can be written as a product of P's involving exchange-clusters of atoms. For example, if P_λ denotes exchange of electrons 1 and 2 between atoms a and b, 2 and 3 between atoms b and c, 5 and 6 between m and n, then we call the triplet (a b c) a linked exchange-cluster; the pair (mn) is also such a linked cluster. If we follow a perturbation method for the evaluation of any property of the solid, then we will in principle obtain contributions due to such exchange-clusters in every order of approximation. These contributions can be ordered according to the largest cluster which they contain : monatomic terms (without exchange), diatomic terms (only pair exchange), triatomic contributions involving triplets of atoms but no larger clusters, etc. With increasing cluster-size we describe the solid in terms of units of increasing numbers of atoms : single atoms, pairs, triplets, etc; this procedure amounts to an increasing delocalization of electrons in the solid.

In this way, a double series expansion is obtained : one, in terms of exchange-clusters of increasing size, and one, in increasing orders of perturbation theory. For molecular solids this procedure may be expected to yield convergent series in both directions. In fact, it is convenient to define molecular solids by the requirement that both the cluster expansion and the perturbation series converge rapidly for any property of interest. Such a solid can be expected to show molecular characteristics to a large extent.

The different possible types of manybody interactions can now be indicated. In the following Table I, we place to the left the exchange-clusters of increasing size, to the right the different orders of perturbation theory. A straight line between left- and right-columns connects a cluster term with the lowest order of perturbation theory in which manybody interactions occur.

Table I. Possible types of manybody interactions



If we use two sets of numbers 1, 2, 3, ..., to characterize a type of manybody effect, of which the first number denotes the cluster-size, the second the order of perturbation theory, then the Axilrod-Teller^{1, 2} - effect is of type 1-3, the second-order (van der Waals) manybody term^{14, 15} of type 2-2, and the Rosen-Shostak^{8, 9}-calculation of type 3-1. The common twobody interactions may also be indicated in this manner : 1-2, i.e. van der Waals forces, and 2-1, i.e., repulsive interactions between closed shells at small interatomic distances (exchange forces).

A GAUSSIAN EFFECTIVE-ELECTRON MODEL

The task is now to evaluate these different types of manybody interactions. In principle, accurate knowledge of atomic wave functions is required to obtain precise results. However, if we have in mind an application to the stability problem for crystals of the heavy rare gases, then the use of a more approximate model may be justified, since the effect can depend sensitively only on some general characteristics of the wave functions ("size" of the atom, plus eventually symmetry properties).

We will simplify the problem by means of the following assumptions :

- 1) only single interatomic exchange of electron pairs is taken into account. Effects due to exchange of two or more pairs of electrons between the same two atoms are therefore not considered;
- 2) contributions due to coupling of inter- and intra-atomic exchange are neglected;
- 3) the electron charge distribution of an atom has spherical symmetry.

The assumptions 1) and 2) must be applied with care. In many cases the overlap integrals between the atomic orbitals of the constituents are not small, implying that higher-order overlap and exchange effects may not be neglected ¹⁷. In the case of rare gas crystals effects due to 1), respectively 1) and 2), were found to be negligible, except for very small interatomic distances, for helium and neon ^{14, 15}. Validity of assumption 3) is somewhat in doubt for atoms of the heavy rare gases, following calculations by Linnett and Poe ¹⁸, but quantitative results are not available.

On the basis of the above three assumptions, the following model can be constructed. We sum over single-exchange effects between all possible pairs of electrons (parallel spins) of two, or three, atoms. The total effect is then replaced by exchange between one "effective" electron on each atom. The problem becomes thus formally the same as that concerning hydrogen atoms with parallel spins. The charge distribution for the effective electron is chosen to be of Gaussian form

17. cf. P.O. Löwdin, Adv. in Phys. 5, 1 (1956), for a general discussion of this difficulty.

18. J.W. Linnett and A.J. Poe, Trans. Far. Soc. 47, 1033 (1951). See also J. Cuthbert and J.W. Linnett, Trans. Far. Soc. 54, 617 (1958).

$$\rho(r) = (\beta/\pi^{1/2})^3 \exp(-\beta^2 r^2); \dots \quad (2)$$

r is the distance from the effective electron to its nucleus, β is a parameter. Values of β for atoms of the heavy rare gases are determined empirically, by calculating second-order dipole interactions between two Gaussian atoms at large distances and comparing the result with an empirical potential function¹⁵. In this way we fit the outer part of the Gaussian distribution. For short-range interactions the inner part of the charge distribution also plays an important rôle, so that it becomes necessary to compare such interactions between Gaussian atoms with the repulsive part of an empirical potential function. Such a comparison will be carried out in a following section.

EXAMPLE : THE EXCHANGE QUADRUPOLE MOMENT OF A PAIR OF ARGON ATOMS

To illustrate the use of the Gaussian model, we calculate the electric quadrupole moment of a pair of argon atoms, a distance R apart. The exchange-repulsion between closed shells will give rise to a small net positive charge in the region between two argon atoms, and a negative charge elsewhere. This effect gives rise to exchange multipole moments of even order, of which we determine the first one, an electric quadrupole moment.

Consider two Gaussian atoms at interatomic distance R . The charge distribution of this pair has cylindrical symmetry about an axis z , coinciding with the direction of R . For such cylindrically symmetric distributions of charge we can define scalar multipole

moments of arbitrary (positive) order ⁵; the first non-vanishing moment is in this case a quadrupole, defined by

$$Q = \langle \sum_i e_i z_i^2 \rangle - \langle \sum_i e_i x_i^2 \rangle ; \quad (3)$$

where the x-axis is perpendicular to \underline{z} , but otherwise arbitrary. For two Gaussian atoms, \underline{a} and \underline{b} , we have two electrons, $\underline{1}$ and $\underline{2}$, and the analogy with the case of two hydrogen atoms with parallel spins makes it possible to write the zero-order wave function as

$$\Psi^{(0)} = \frac{1}{\sqrt{2(1-\Delta^2)}} \{ \varphi_a(1) \varphi_b(2) - \varphi_a(2) \varphi_b(1) \} , \quad (4)$$

where $\varphi^2 = \rho$, the Gaussian charge density of an atom, and Δ is the overlap integral, $\Delta = \int \varphi_a \varphi_b d\tau$. The direct terms in $\Psi^{(0)}$ give, of course, no contribution to Q or to any other permanent multipole moment, so that we are left with the exchange terms (omitting normalization) $-2 \varphi_a(1) \varphi_b(1) \varphi_a(2) \varphi_b(2)$.

We denote the z-coordinates of the position vectors of electrons 1 and 2, with respect to the center of the line connecting the two nuclei, by z_1 and z_2 , respectively. Then we obtain :

$$\langle \sum_i e_i z_i^2 \rangle = \left\{ 4e i_3 \Delta - 4e (R/2)^2 \Delta^2 \right\} / 2 (1 - \Delta^2),$$

where

$$i_3 = \int z^2 \varphi_a \varphi_b d\tau ; \quad (5)$$

$$\langle \sum_i e_i x_i^2 \rangle = 4 e \dot{I}_2 \Delta / 2 (1 - \Delta^2)$$

with

$$I_2 = \int x^2 \varphi_a \varphi_b d\tau \quad (6)$$

The expression for the scalar quadrupole moment of the pair (a b) of argon atoms becomes with (3), (5) and (6),

$$\begin{aligned} Q &= \langle \sum_i e_i z_i^2 \rangle - \langle \sum_i e_i x_i^2 \rangle = \\ &= \{ 4 e \Delta (\dot{I}_3 - \dot{I}_2) - 4 e \Delta^2 (R/2)^2 \} / 2 (1 - \Delta^2) \end{aligned} \quad (7)$$

For a Gaussian distribution $\dot{I}_3 = \dot{I}_2$, so that then

$$Q = -2e \frac{\Delta^2}{1 - \Delta^2} (R/2)^2. \quad (8)$$

This quadrupole moment is the same as that caused by an effective negative point-charge $-(\delta e) = -e \frac{\Delta^2}{1 - \Delta^2}$ at nucleus a, the same charge at nucleus b, and a positive charge $2(\delta e)$ at the center between the two nuclei.

Values of $\Delta^2/(1 - \Delta^2)$ can be determined with the help of those of the parameter β in the Gaussian distribution function, for the heavy rare gases¹⁵. For nearest neighbors in solid argon $\Delta^2/(1 - \Delta^2) = 0.06$, and $R/2 = 1.92 \text{ \AA}$. The resulting value for the scalar quadrupole moment of a pair of nearest-neighbor argon atoms is then

$$Q = 2.14 \times 10^{-26} \text{ e.s.u} = 0.45 \times 10^{-16} \text{ e cm}^2,$$

i. e., a value of the same order of magnitude as for a nitrogen molecule. This large value is not due to a large displacement of charge, but in the first place to the large value of the distance between two argon atoms, which enters as the square in the expression for the quadrupole moment (compare a nitrogen molecule : $R/2 = 0.55 \text{ \AA}$).

In view of the approximations which are inherent in this type of model, quantitative conclusions do not seem to be justified. The result indicates, however, that effects due to diatomic exchange-clusters of heavy rare gas atoms may be significant for the determination of some solid state properties*.

THE TRIATOMIC-FIRST ORDER (3-1) MANYBODY EFFECT

The task is now to evaluate the different possible types of many-body interactions in first, second and third orders of perturbation theory. The remainder of this paper is devoted to a calculation of the 3-1-effect,

*) This quadrupole effect may possibly be observed by means of spectra emitted by trapped radicals in rare gas matrices, e.g. from excited nitrogen atoms or excited alkali atoms in solid argon.

involving a cluster of three atoms, in first order of perturbation theory. It was mentioned earlier that P. Rosen and Shostak computed such interactions for three helium atoms. Helium is, however, of no direct interest as far as its crystal structure is concerned, and a direct extension of the methods used by these authors to the heavy rare gases would be very complicated, since detailed knowledge of the wave functions is required. We will, therefore, make use of the Gaussian model, one effective electron per atom, with a charge density given by (2), and variable β .

Consider such a triangle (a b c) of atoms. The zero-order wave function is (Slater determinant)

$$\psi^{(0)} = \frac{1}{\sqrt{3! (1 - \Delta^2_{abc})}} \text{Det} \{ \varphi_a(1) \varphi_b(2) \varphi_c(3) \}, \quad (9)$$

with

$$\Delta^2_{abc} = \Delta^2_{ab} + \Delta^2_{ac} + \Delta^2_{bc} - 2 \Delta_{ab} \Delta_{ac} \Delta_{bc}, \quad (10)$$

The perturbation Hamiltonian, H'_{abc} , can be written as

$$H'_{abc} = H'_{ab} + H'_{ac} + H'_{bc}.$$

For the first-order energy we have to evaluate

$$E_1 = \langle H'_{abc} \rangle = \langle H'_{ab} \rangle + \langle H'_{ac} \rangle + \langle H'_{bc} \rangle.$$

After substituting the expressions for H'_{ab} and $\psi^{(0)}$ into E_1 , the following result is obtained :

$$\begin{aligned}
 \langle H'_{ab} \rangle / e^2 = & \frac{1}{R_{ab}} - 2 \frac{1 - \frac{1}{2} (\Delta_{ac}^2 + \Delta_{bc}^2)}{1 - \Delta_{abc}^2} G_{aa(b)} + \\
 & + 2 \frac{\Delta_{ab} - \Delta_{ac} \Delta_{bc}}{1 - \Delta_{abc}^2} G_{ab(a)} + \frac{\Delta_{ac} - \Delta_{ab} \Delta_{bc}}{1 - \Delta_{abc}^2} G_{ac(b)} + \\
 & + \frac{\Delta_{bc} - \Delta_{ab} \Delta_{ac}}{1 - \Delta_{abc}^2} G_{bc(a)} + \frac{1}{1 - \Delta_{abc}^2} (A_{abab} - A_{aabb}) + \\
 & + \left(\frac{\Delta_{ac}}{1 - \Delta_{abc}^2} \right) (A_{abbc} - A_{abcb}) + \left(\frac{\Delta_{bc}}{1 - \Delta_{abc}^2} \right) (A_{aabc} - A_{abac}) \quad (11)
 \end{aligned}$$

where the symbols G and A are abbreviations for the following integrals

$$G_{ab(c)} = \int \frac{\varphi_a \varphi_b}{r_c} d\tau \quad ; \quad G_{aa(b)} = \int \frac{\varphi_a \varphi_a}{r_b} d\tau \quad ; \text{ etc.,}$$

$$\begin{cases} r_c & = \text{distance between an electron and nucleus of atom } \underline{c}, \\ r_b & = \text{distance between an electron and nucleus of atom } \underline{b}. \end{cases}$$

$$A_{abac} = \iint \frac{\varphi_a(1) \varphi_b(2) \varphi_a(1) \varphi_c(2)}{r_{12}} d\tau_1 d\tau_2 ;$$

$$A_{aabc} = \iint \frac{\varphi_a(1) \varphi_a(2) \varphi_b(1) \varphi_c(2)}{r_{12}} d\tau_1 d\tau_2 ;$$

etc., r_{12} = distance between electrons 1 and 2.

The first-order energy between a and b, without c present, is

$$\begin{aligned} \langle H'_{ab} \rangle^{(0)} / e^2 &= \frac{1}{R_{ab}} - \frac{1}{1 - \Delta_{ab}^2} [2G_{aa(b)} - 2\Delta_{ab} G_{ab(a)} - \\ &- (A_{abab} - A_{aabb})], \end{aligned} \quad (12)$$

The threebody component of $\langle H'_{ab} \rangle / e^2$, namely

$$\{ \langle H'_{ab} \rangle - \langle H'_{ab} \rangle^{(0)} \} / e^2,$$

is obtained by subtracting (12) from (11). We do not need any further equations, since $\langle H'_{ac} \rangle$, for example, is obtained from (11) by replacing b by c.

The integrals G and A have, for Gaussian distributions of charge, been evaluated by Boys¹⁹. For the atomic wave functions we take

19. S.F. Boys, Proc. Roy. Soc. A200, 542 (1950).

$$\varphi = \rho^{1/2} = (\beta / \pi^{1/2})^{3/2} \exp(-\beta^2 r^2/2)$$

It is convenient to use the following abbreviation

$$F(x) = \frac{1}{\sqrt{x}} \int_0^{\sqrt{x}} e^{-y^2} dy ;$$

also, we denote by $R_{a(bc)}$ the length of the line connecting the nucleus of atom \underline{a} with the center of the line R_{bc} , etc. The following table contains a list of the integrals occurring in the equation for E_1 .

Table II. List of integrals for E_1

<u>Integral</u>	<u>Value for Gauss-distribution</u>
Δ^2_{ab}	$\exp(-\beta^2 R^2_{ab}/2)$
Δ^2_{ac}	$\exp(-\beta^2 R^2_{ac}/2)$
Δ^2_{bc}	$\exp(-\beta^2 R^2_{bc}/2)$
$\Delta^2_{abc} = \Delta^2_{ab} + \Delta^2_{ac} + \Delta^2_{bc} - 2\Delta_{ab} \Delta_{ac} \Delta_{bc}$	

$G_{aa(b)} = G_{bb(a)}$	$(2\beta/\sqrt{\pi}) F(\beta^2 R^2_{ab})$
$G_{ab(a)} = G_{ab(b)}$	$(2\beta/\sqrt{\pi}) \Delta_{ab} F(\beta^2 R^2_{ab}/4)$
$G_{bc(a)}$	$(2\beta/\sqrt{\pi}) \Delta_{bc} F(\beta^2 R^2_{a(bc)})$
$G_{ac(b)}$	$(2\beta/\sqrt{\pi}) \Delta_{ac} F(\beta^2 R^2_{b(ac)})$
A_{abab}	$\beta \sqrt{2/\pi} F(\beta^2 R^2_{ab}/2)$
A_{aabb}	$\beta \sqrt{2/\pi} \Delta^2_{ab}$
A_{abac}	$\beta \sqrt{2/\pi} \Delta_{bc} F(\beta^2 R^2_{a(bc)}/2)$
A_{abcb}	$\beta \sqrt{2/\pi} \Delta_{ac} F(\beta^2 R^2_{b(ac)}/2)$
A_{aabc}	$\beta \sqrt{2/\pi} \Delta_{ab} \Delta_{ac} F(\beta^2 R^2_{bc}/8)$
A_{abbc}	$\beta \sqrt{2/\pi} \Delta_{ab} \Delta_{bc} F(\beta^2 R^2_{ac}/8)$

MACHINE CALCULATIONS

The computations were carried out on the digital computer Bull Gamma AET (word-length : 12 digits; memory access : 172 microseconds; type of storage : magnetic drum of 8192 memories). After calculating the arguments of the F- and Δ -functions for various triangular configurations, these functions were evaluated by interpolation, using "Tables of the Error Function and its Derivative" (Nat. Bureau of Standards, Washington, 1953). The interpolation was carried to the fifth term of a Taylor expansion; this

appeared sufficient for the accuracy desired. The intermediate results were transmitted by punchcards to the main program, i. e., the computation of $\langle H'_{abc} \rangle$, $\langle H'_{abc} \rangle^{(0)}$, their difference, and the relative threebody component of the first-order interactions, for values of βR from 1.5 to 3.5, in intervals of 0.1, for each triangular configuration.

For values of βR larger than about 3 the results are somewhat irregular, since the different terms in equations (11) and (12) are then very small, and the sums and differences of a large number of such terms have to be determined. The program was devised in such a way that different triangles require only slight modifications.

RESULTS FOR SOME SPECIAL TRIANGLES

The threebody, first-order interaction energies were evaluated for a number of special triangles, among others, an equilateral triangle, a 120° -symmetric array and a linear symmetric array. These three types of triangles occur among those formed by a central atom and two of its twelve nearest neighbors in the cubic, and hexagonal, close-packed lattices. The relative threebody contribution is

$$\frac{\langle H'_{abc} \rangle - \langle H'_{abc} \rangle^{(0)}}{\langle H'_{abc} \rangle^{(0)}} \quad , \quad (13)$$

where

$$\langle H'_{abc} \rangle^{(0)} = \langle H'_{ab} \rangle^{(0)} + \langle H'_{ac} \rangle^{(0)} + \langle H'_{bc} \rangle^{(0)} \quad , \text{ a sum of first-}$$

order energies over three isolated pairs of atoms. The relative three-body component (13) is a function only of the dimensionless parameter βR , where R is the smallest distance between neighbors in the triangle. Calculations were performed for the three types of triangles with $\beta R = 1.5; 1.6, \dots; 3.5$, in intervals of 0.1. This range covers the βR -values for neon, argon, krypton and xenon, which are 3.44, 2.40, 2.10 and 1.99, respectively ¹⁵. The results are collected in the following Figure 1.

Fig. 1 : Relative threebody, first-order interactions for an equilateral triangle, a 120° -symmetric and a linear symmetric array, as a function of βR .

The main characteristics of the threebody interactions are :

- 1) Equilateral triangle . The relative threebody interaction is practically independent of βR , i. e. of the size of the triangle (at constant β). It amounts to about 20 percent and its sign is minus, meaning that the total first-order interaction is weaker (less repulsive) than obtained on the basis of an additive sum-over-pairs. The sign agrees with the result obtained by P. Rosen for three helium-atoms;
- 2) 120° -symmetric array. For this configuration the relative threebody component is only at most 5 percent of the additive first-order interactions and its sign is plus, signifying slightly enhanced repulsion compared with the sum over three isolated pairs;

3) Linear symmetric array. The relative threebody interaction is very nearly decreasing linearly with increasing βR , from 20 percent at $\beta R = 1.5$ to a few percent at $\beta R = 3$. Its sign is plus, which means that the effect enhances the repulsion between the three atoms, compared with an additive sum-over-pairs. The sign agrees with that obtained by P. Rosen and by Shostak for three helium atoms.

VALIDITY OF GAUSSIAN MODEL AT SMALL DISTANCES

At small interatomic distances the inner part of the charge distribution plays an important rôle in the determination of the repulsive interactions between closed shells of electrons. Since the values for the parameter β in the Gaussian distribution were determined empirically from a comparison with long - range interactions, it is of interest to check whether or not β changes appreciably with decreasing distance between the atoms. To this end we use the repulsive part of a modified Buckingham potential,

$$E(r) = \frac{\epsilon}{1 - (6/a)} (6/a) \exp a (1 - R/R_0),$$

with values of ϵ , a , and R_0 for neon, argon, krypton and xenon as given by Hirschfelder, Curtiss and Bird²⁰ as an empirical basis, and

20. Hirschfelder, Curtiss and Bird, Molecular Theory of Gases and Liquids (John Wiley and Sons, Inc. New York, 1954) Chap. 12.

compare the results with $\langle H'_{ab} \rangle^{(0)}$, eq. (12), taking for β the values for the heavy rare gases, and varying R . The results of this comparison are given in the following Figure 2.

Fig. 2 : Comparison between repulsive part of modified Buckingham potential and $\langle H'_{ab} \rangle^{(0)}$ for a Gaussian distribution, for the heavy rare gases, as function of interatomic distance R .

It is seen from Figure 2 that the Gaussian model yields excellent values for the repulsive potential between two neon atoms, but that with increasing atomic weight the two curves deviate more and more. This implies that β for argon, krypton and xenon increases somewhat as R decreases, indicating a certain "quenching" of the three-body-effect. It should be remembered, however, that with decreasing R multiple-exchange effects become more and more important, rendering the single-exchange model less and less valid. For neon, argon, krypton and xenon the nearest neighbor distances in the crystals are 3.20 Å, 3.84 Å, 3.94 Å, and 4.37 Å, respectively.

CONCLUSIONS

- 1) It is possible to classify the various manybody interactions between atoms in "molecular solids" on the basis of a double series expansion; one, in terms of linked exchange-clusters of increasing size,

and one, in increasing orders of perturbation theory. Molecular solids may then be defined by the requirement that both expansions converge rapidly;

2) With the help of a Gaussian effective-electron model, the triatomic-first-order threebody interactions given by P. Rosen and Shostak for helium atoms, may be extended to the heavy rare gases. Both for an equilateral triangle and a linear symmetric array the sign of the relative threebody interaction agrees with previous results for helium;

3) For a single triangular configuration the relative threebody interaction may amount to 20 percent of the additive first-order energy;

4) Values for the parameter β of the Gaussian distribution, obtained from a comparison with long-range interactions, give excellent values for short-range forces between two neon atoms. For argon, krypton and xenon β appears to increase somewhat with decreasing interatomic distances.

C. THREEBODY INTERACTIONS BETWEEN RARE GAS ATOMS IN FIRST-ORDER PERTURBATION THEORY

Compilation of Results

General

The method used for the evaluation of threebody interactions in first-order of perturbation theory is that developed in section B. For completeness, some of the general equations will be repeated from this section.

The triatomic-first-order (3-1) effect

To evaluate the 3-1 effect for a triangle of rare gas atoms, use is made of a Gaussian effective-electron model. The total effect for all electrons of the three atoms is replaced by that due to one "effective" electron on each atom. The charge distribution of the effective electron is chosen to be of Gaussian form :

$$\rho(r) = (\beta/\pi)^{1/2} \exp(-\beta^2 r^2) \quad (14)$$

where β is a parameter which can be determined empirically.

Consider such a triangle of three Gaussian atoms a, b and c, each with one electron (spins parallel). The electrostatic interaction between the three atoms can be written as :

$$H'_{abc} = H'_{ab} + H'_{ac} + H'_{bc} , \quad (15)$$

whereas the first-order energy has the form :

$$\langle H'_{abc} \rangle = \langle H'_{ab} \rangle + \langle H'_{ac} \rangle + \langle H'_{bc} \rangle , \quad (16)$$

with :

$$\langle H'_{abc} \rangle = \iiint \Psi_0^* H'_{abc} \Psi_0 \, d\tau_1, d\tau_2, d\tau_3, \text{ etc.}$$

The zero-order wave function Ψ_0 is a Slater determinant :

$$\Psi_0 = \frac{1}{\sqrt{3! (1 - \Delta_{abc}^2)}} \text{Det} \left\{ \varphi_a(1) \varphi_b(2) \varphi_c(3) \right\} , \quad (17)$$

where φ_a, φ_b and φ_c are (antisymmetrized) ground-state wave functions for the atoms a, b and c, and

$$\Delta_{abc}^2 = \Delta_{ab}^2 + \Delta_{ac}^2 + \Delta_{bc}^2 - 2\Delta_{ab}\Delta_{ac}\Delta_{bc} ,$$

with

$$\Delta_{ab} = \int \varphi_a^* \varphi_b d\tau, \text{ the overlap integral between } \underline{a} \text{ and } \underline{b}, \text{ etc.}$$

If we denote by $\langle H'_{abc} \rangle^{(0)}$ the simple sum of first-order interactions for three isolated pairs of atoms, then

$\langle H'_{abc} \rangle - \langle H'_{abc} \rangle^{(0)}$ gives the threebody component of the first-order energy. It is only necessary to compute $\langle H'_{ab} \rangle$ and $\langle H'_{ab} \rangle^{(0)}$, since the remaining terms are obtained by changing indices. The results are :

$$\begin{aligned} \frac{\langle H'_{ab} \rangle}{e^2} &= \frac{1}{R_{ab}} - 2 \frac{1 - \frac{1}{2} (\Delta_{ac}^2 + \Delta_{bc}^2)}{1 - \Delta_{abc}^2} G_{aa(b)} + \\ &+ 2 \frac{\Delta_{ab} - \Delta_{ac} \Delta_{bc}}{1 - \Delta_{abc}^2} G_{ab(a)} + \frac{\Delta_{ac} - \Delta_{ab} \Delta_{bc}}{1 - \Delta_{abc}^2} G_{ac(b)} + \\ &+ \frac{\Delta_{bc} - \Delta_{ab} \Delta_{ac}}{1 - \Delta_{abc}^2} G_{bc(a)} + \frac{1}{1 - \Delta_{abc}^2} (A_{abab} - A_{aabb}) + \\ &+ \frac{\Delta_{ac}}{1 - \Delta_{abc}^2} (A_{abbc} - A_{abcb}) + \frac{\Delta_{bc}}{1 - \Delta_{abc}^2} (A_{aabc} - A_{abac}), \end{aligned} \quad (18)$$

where the symbols G and A are abbreviations for the integrals

$$G_{ab(c)} = \int \frac{\varphi_a \varphi_b}{r_c} d\tau ; \quad G_{aa(b)} = \int \frac{\varphi_a \varphi_a}{r_b} d\tau ; \text{ etc.}$$

$$\begin{cases} r_c = \text{distance between an electron and nucleus of atom c,} \\ r_b = \text{distance between an electron and nucleus of atom b.} \end{cases}$$

$$A_{abac} = \iint \frac{\varphi_a(1)\varphi_b(2)\varphi_a(1)\varphi_c(2)}{r_{12}} d\tau_1 d\tau_2 ;$$

$$A_{aabc} = \iint \frac{\varphi_a(1)\varphi_a(2)\varphi_b(1)\varphi_c(2)}{r_{12}} d\tau_1 d\tau_2 ; \text{ etc.}$$

r_{12} = distance between electrons 1 and 2.

The first-order energy between a and b, without c present, is :

$$\langle H'_{ab} \rangle^{(0)}/e^2 = \frac{1}{R_{ab}} - \frac{1}{1-\Delta_{ab}^2} [2G_{aa(b)} - 2\Delta_{ab}G_{ab(a)} - (A_{abab} - A_{aabb})] \quad (19)$$

Since the φ 's are real, we can take :

$$\varphi(r) = \rho(r)^{1/2} = (\beta/\pi)^{1/2} \exp(-\beta^2 r^2/2), \quad (20)$$

It is also convenient to introduce the abbreviation :

$$F(z) = \frac{1}{\sqrt{z}} \int_0^{\sqrt{z}} e^{-\alpha^2} d\alpha ; \quad (21)$$

F is related to the error function $\text{erf}(y)$ or $H(y)$,

$$H(y) = \frac{2}{\sqrt{\pi}} \int_0^y e^{-\alpha^2} d\alpha$$

as follows :

$$F(y^2) = \frac{1}{y} \int_0^y e^{-\alpha^2} d\alpha = \frac{\sqrt{\pi}}{2y} H(y), \quad (22)$$

The following Table II contains the different types of integrals, with their values for a Gaussian distribution function.

TABLE II

List of Integrals for the 3-1 Effect

<u>Integral</u>	<u>Value for Gauss distribution</u>
Δ_{ab}^2	$\exp(-\beta^2 R_{ab}^2/2)$
Δ_{ac}^2	$\exp(-\beta^2 R_{ac}^2/2)$
Δ_{bc}^2	$\exp(-\beta^2 R_{bc}^2/2)$
$\Delta_{abc}^2 = \Delta_{ab}^2 + \Delta_{ac}^2 + \Delta_{bc}^2 - 2\Delta_{ab}\Delta_{ac}\Delta_{bc}$	
$G_{aa(b)} = G_{bb(a)}$	$(2\beta/\sqrt{\pi}) F(\beta^2 R_{ab}^2)$
$G_{ab(a)} = G_{ab(b)}$	$(2\beta/\sqrt{\pi}) F(\beta^2 R_{ab}^2/4)$
$G_{bc(a)}$	$(2\beta/\sqrt{\pi}) \Delta_{bc} F(\beta^2 R_{a(bc)}^2)$
$G_{ac(b)}$	$(2\beta/\sqrt{\pi}) \Delta_{ac} F(\beta^2 R_{b(ac)}^2)$
A_{abab}	$\beta\sqrt{2/\pi} F(\beta^2 R_{ab}^2/2)$
A_{aabb}	$\beta\sqrt{2/\pi} \Delta_{ab}^2$
A_{abac}	$\beta\sqrt{2/\pi} \Delta_{bc} F(\beta^2 R_{a(bc)}^2/2)$
A_{abcb}	$\beta\sqrt{2/\pi} \Delta_{ac} F(\beta^2 R_{b(ac)}^2/2)$
A_{aabc}	$\beta\sqrt{2/\pi} \Delta_{ab} \Delta_{ac} F(\beta^2 R_{bc}^2/8)$
A_{abbc}	$\beta\sqrt{2/\pi} \Delta_{ab} \Delta_{bc} F(\beta^2 R_{ac}^2/8)$
$R_{a(bc)} = \text{distance between } \underline{a} \text{ and the middle of the line } R_{bc}; \text{ etc.}$	

MACHINE CALCULATIONS

The calculations were carried out on the digital computer BULL GAMMA AET. The general machine features are :

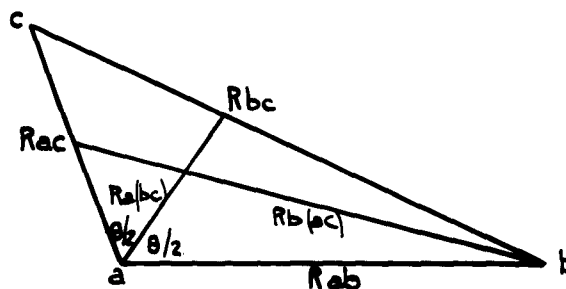
<u>word-length</u>	: 12 digits (binary commands)
<u>instructions per word</u>	: 3
<u>operation times</u>	: memory access 172 μ s
<u>type of storage</u>	: magnetic drum of 8192 memories
<u>input-output</u>	:

punch cards equipment : speed 175 cards per minute
 cards-reader equipment : speed 150 cards per minute
 printer : speed 150 lines per minute.

programming : in machine language or in symbolic programming system (AP2).

Evaluation of eqs. (18) and (19)

The threebody first-order effect was evaluated for several different types of isosceles triangles (a b c).



All distances are made dimensionless through multiplication with the Gaussian parameter β . We need the following quantities :

$$\beta R_{ab} = \beta R_{ac}$$

$$\beta R_{bc} = u \beta R_{ab}$$

$$\beta R_{a(bc)} = \beta R_{ab} \sqrt{1 - \frac{u^2}{4}} = v \beta R_{ab}$$

$$\beta R_{b(ac)} = \frac{\beta R_{ab}}{2} \sqrt{1 + 2 u^2} = w \beta R_{ab}$$

$$\text{where } u = 2 \sin \theta/2, \quad v = \sqrt{1 - \frac{u^2}{4}}, \quad w = (\sqrt{1 + 2 u^2})/2.$$

The quantity $x = \beta R_{ab}$ can be taken as parameter, in terms of which :

$$\langle H'_{ab} \rangle / \beta e^2 \quad \text{and} \quad \langle H'_{ab} \rangle^{(0)} / \beta e^2$$

are given for any particular triangle. A range of values for x was chosen between 1.5 and 3.5, in intervals of 0.1.

The equations to be evaluated are polynomials consisting of exponential terms and error functions :

Exponentials :

$$(A) \quad \Delta_{ab}^2 = \exp(-x^2/2)$$

$$(B) \quad \Delta_{ac}^2 = \exp(-x^2/2)$$

$$(C) \quad \Delta_{bc}^2 = \exp(-ux^2/2)$$

$$\Delta_{abc}^2 = \Delta_{ab}^2 + \Delta_{ac}^2 + \Delta_{bc}^2 - 2 \Delta_{ab} \Delta_{ac} \Delta_{bc}.$$

Error functions : The G- and A-integrals assume the following simple forms :

$$(D) \quad G_{aa(b)}/\beta = (2/\sqrt{\pi}) F(x^2) = (1/x) H(x)$$

$$(E) \quad G_{ab(a)}/\beta = (2/\sqrt{\pi}) \Delta_{ab} F(x^2/4) = (2/x) H(x/2) \Delta_{ab}$$

$$(F) \quad G_{bc(a)}/\beta = (2/\sqrt{\pi}) \Delta_{bc} F(v^2 x^2) = (1/vx) H(vx) \Delta_{bc}$$

$$(G) \quad G_{ac(b)}/\beta = (2/\sqrt{\pi}) \Delta_{ac} F(w^2 x^2) = (1/wx) H(wx) \Delta_{ac}$$

$$(H) \quad A_{abab}/\beta = (1/\sqrt{2}) (2/\sqrt{\pi}) F(x^2/2) = (1/x) H(x/\sqrt{2})$$

$$(J) \quad A_{aabb}/\beta = \sqrt{2/\pi} \Delta_{ab}^2$$

$$(K) \quad A_{abac}/\beta = (1/\sqrt{2}) (2/\sqrt{\pi}) \Delta_{bc} F(v^2 x^2/2) = (1/vx) H(vx/\sqrt{2}) \Delta_{bc}$$

$$(L) \quad A_{abcb}/\beta = (1/\sqrt{2}) (2/\sqrt{\pi}) \Delta_{ac} F(w^2 x^2/2) = (1/wx) H(wx/\sqrt{2}) \Delta_{ac}$$

$$(M) \quad A_{aabc}/\beta = (1/\sqrt{2}) (2/\sqrt{\pi}) \Delta_{ab} \Delta_{ac} F(u^2 x^2/8) = (2/ux) H(ux/2\sqrt{2}) \Delta_{ab} \Delta_{ac}$$

$$(N) \quad A_{abbc}/\beta = (1/\sqrt{2}) (2/\sqrt{\pi}) \Delta_{ab} \Delta_{bc} F(x^2/8) = (2/x) H(x/2\sqrt{2}) \Delta_{ab} \Delta_{bc}$$

Symbolic Programs :

It appeared essential to employ a floating point program. The programming was carried out in small part in machine language and the rest in symbolic language which reduced the work considerably. The computations can be subdivided into the following independent parts :

a) Calculation of arguments of the G- and A-integrals. This very short program was primarily intended as a check on the symbolic program AP2.

b) Calculation of the exponentials and error functions :

$$H'(x) = (2/\sqrt{\pi}) \exp(-x^2); H(x) = (2/\sqrt{\pi}) \int_0^x e^{-\alpha^2} d\alpha.$$

First, $H'(x)$ was computed by means of a subprogram (Bull) with an error less than 1 in the 10th decimal place. Then, $H(x)$ was evaluated by direct integration of $H'(x)$ with the help of Simpson's method :

$$H(x_{n+1}) = H(x_{n-1}) + \frac{h}{3} [H'(x_{n-1}) + 4 H'(x_n) + H'(x_{n+1})] ,$$

with an error $\leq H^{(V)} h^5 / 90$;

$$\int_0^{*2m} H'(x) dx = \frac{h}{3} [H'(0) + 4H'(1) + 2H'(2) + 4H'(3) + \dots + 4H'_{2m-1} + H'_{2m}] ,$$

with an error $\leq mH^{(V)} h^5 / 90$.

This method had, however, to be abandoned, since the necessary high precision could not be reached.

A second program was based on interpolation between values given in "Tables of the Error Function and its Derivative" (National Bureau of Standards, Washington D.C., 1953). These tables give values for $H'(x)$ and $H(x)$ to 15 decimals in intervals of 10^{-4} for x between 0 and 1, and in intervals of 10^{-3} for x between 1 and 5.6.

It appeared more advantageous to employ a high-order interpolation formula and fewer tabulated values than inversely. This avoided the necessity of storing long lists of tables in the machine. A Taylor-expansion to fifth order was used and appeared to yield satisfactory precision.

$$H(x) = H(x_0) + ph H'(x_0) + \frac{(ph)^2}{2!} H''(x_0) + \dots + \frac{(ph)^5}{5!} H^{(V)}(x_0),$$

with

$$H''(x_0) = -2x_0 H'(x_0);$$

$$H'''(x_0) = (4x_0^2 - 2) H'(x_0), \text{ etc.}$$

where

$$ph = x - x_0 \text{ and } h = x_1 - x_0 = x_2 - x_1 = \text{etc. with } p \leq 1/2.$$

In this way, values for $H(x)$ were obtained which were accurate to 9 or 10 decimal places, depending upon the range of values for x . All results were stored on punchcards for use in the main program.

Main Program

In the first part of the main program, four different types of isosceles triangles were considered, characterized by :

$$u = \sqrt{8/3}, \quad \theta \sim 110^\circ, \quad \text{triangle I};$$

$$u = \sqrt{11/3}, \quad \theta \sim 146^\circ, \quad \text{triangle II};$$

$$u = 2, \quad \theta = 180^\circ, \quad \text{triangle III};$$

$$u = \sqrt{3}, \quad \theta = 120^\circ, \quad \text{triangle IV}.$$

Each triangle was considered in two different configurations :

i) R_{ab} as one of the two equal sides of the triangle;

ii) R_{ab} as the third side of the triangle.

In case i) the results for $\langle H'_{ab} \rangle / \beta e^2$ and $\langle H'_{ab} \rangle^{(0)} / \beta e^2$ were abbreviated as A_1, B_1 , respectively, whereas in case ii) these results are denoted by A_2, B_2 .

For each of the four triangles, and for each value of the parameter $x = \beta R_{ab}$ the following quantities were calculated :

triangle I $A_{I_1}, A_{I_2}, B_{I_1}, B_{I_2}; R_I$.

triangle II $A_{II_1}, A_{II_2}, B_{II_1}, B_{II_2}; R_{II}$. etc.,

with
$$R_n = \frac{2 A_{n1} + A_{n2}}{2 B_{n1} + B_{n2}} .$$

The ratio R_n gives the relative threebody component

$$\frac{\langle H'_{abc} \rangle - \langle H'_{abc} \rangle^{(0)}}{\langle H'_{abc} \rangle} ,$$

for a triangle of type \underline{n} .

It was found that for values of x larger than 3 the results become more or less irregular. This is due to the fact that then the H-functions are practically equal to $\sqrt{2/\pi}$ and the H' equal to zero; partial results may become as small as one in the ninth or tenth decimal place. It would, nonetheless, have been possible to retain high accuracy also for this range of values for x by using a double-precision calculation (to 22 decimal places). This was, however, considered unwise since it would have prolonged the calculation times very considerably.

In the second part of the program, two more types of triangles were evaluated, characterized by :

$$u = 1, \quad \theta = 60^\circ, \quad \text{triangle V}$$

$$u = 2, \quad \theta = 90^\circ, \quad \text{triangle VI,}$$

which was possible without principal modifications of the program. The results were plotted as function of θ , and proved to exhibit regular behaviour.

In Fig. 1, (section B), the relative threebody, first-order interactions for an equilateral triangle, a 120° -symmetric and a linear symmetric array are plotted as a function of $x = \beta R$. In Table III detailed results are given for $A = \langle H'_{ab} \rangle / \beta e^2$ for the two different configurations of each triangle I, II, III, IV, V and VI ($A_V = A_{V_1}$), as well as the twobody interaction energy B_V , for x between 1.5¹ and 3.5².

Secondary Programs

The foregoing results, transferred to punchcards, were applied to a determination of first-order, threebody interactions between triangles of atoms formed by a central atom and a pair of nearest neighbors in the face-centered cubic (fcc) and hexagonal close-packed (hcp) structures.

The total threebody interaction may be written as

$$N (\beta e^2) (E_{a\Delta})_{hcp} \quad \text{and} \quad N (\beta e^2) (E_{a\Delta})_{fcc},$$

where N is the total number of atoms in the crystal, e is the electron charge, and $E_{a\Delta}$ is the total threebody interaction for a central atom (a) and its twelve nearest neighbors. The expressions for $E_{a\Delta}$ are :

$$\begin{aligned} (E_{a\Delta})_{hcp} = & 24 A_V + 18 (2 A_{IV_1} + A_{IV_2}) + 3 (2 A_{III_1} + A_{III_2}) + \\ & + 12 (2 A_{VI_1} + A_{VI_2}) + 3 (2 A_{I_1} + A_{I_2}) + 6 (2 A_{II_1} + A_{II_2}) ; \end{aligned}$$

the roman numerals refer to the different types of triangles. In the case of an equilateral triangle (type V) there is, of course, no distinction to be made between A_{V_1} and A_{V_2} , or between B_{V_1} and B_{V_2} .

$$(E_{a\Delta})_{fcc} = 24 A_V + 18 (2 A_{IV_1} + A_{IV_2}) + 3 (2 A_{III_1} + A_{III_2}) + \\ + 12 (2 A_{VI_1} + A_{VI_2}) + 3 (2 A_{III_1} + A_{III_2}) + 6 (2 A_{IV_1} + A_{IV_2}) .$$

The terms have been arranged in such a way that the first four are the same between the hcp- and fcc-structures, whereas the last two terms are different.

On the other hand, the total twobody interaction is

$$N (\beta e^2) E_{a-b} , \quad \text{with } E_{a-b} = 6 B_V .$$

No distinction has to be made between the twobody interactions in the hcp- and fcc-lattices, since, as far as a central atom and its twelve nearest neighbors are concerned, these interactions are the same, at the same value of $\underline{x} = \beta R$, for the two structures.

The following quantities were calculated as functions of \underline{x} :

$$(E_{a\Delta})_{hcp} ; (E_{a\Delta})_{fcc} ; (E_{a\Delta})_{hcp} - (E_{a\Delta})_{fcc} ,$$

together with ratios

$$(E_{a\Delta})_{hcp} / E_{a-b} \quad \text{and} \quad (E_{a\Delta})_{fcc} / E_{a-b} ;$$

the latter quantities give the relative contributions of first-order, three-body interactions for the two lattices, as a function of $x = \beta R$. Detailed results are given in Table IV.

A final subprogram was used to check the validity of the Gaussian model at small interatomic distances. To this end, the repulsive part of the modified Buckingham-potential,

$$\frac{\epsilon}{1 - (6/a)} \left(\frac{6}{a} \right) e^{a(1-R/R_0)} ,$$

with ϵ , a and R_0 given parameters for neon, argon, krypton and xenon, was compared with the first-order interaction between two Gaussian atoms, $(\beta e^2) B_V$, as a function of βR , R being the distance between the two atoms. Fig. 2 gives the results of this comparison (section B).

TABLE III
First-order, threebody interactions, in units of βe^2 , for different types
of triangles, as function of $x = \beta R$.

$x = \beta R$	A_{I_1}	A_{I_2}	A_{II_1}	A_{II_2}
1.5	- 0, 0055905470	0, 0056896850	0, 0154010910	0, 0125013630
1.6	- 33092160	47516250	118825250	83468750
1.7	- 18704720	37976390	88117130	54072510
1.8	- 10039780	29064250	63053970	33937720
1.9	- 5080635	21330000	43636795	20625360
2.0	- 2403335	15037280	29242028	12137400
2.1	- 1054713	10202158	18983812	6917990
2.2	- 432078	6673254	11937916	3820609
2.3	- 176348	4215124	7267477	2045305
2.4	- 87712	2574916	4278236	1061741
2.5	- 63915	1523233	2431445	534633
2.6	- 58810	873607	1330894	261172
2.7	- 54820	486280	699200	123855
2.8	- 47958	262872	350604	56960
2.9	- 38790	138161	166398	25441
3.0	- 29267	70585	73671	11031

TABLE III (continued)

First-order, threebody interactions, in units of βe^2 , for different types of triangles, as function of $x = \beta R$.

$x = \beta R$	A_{III_1}	A_{III_2}	A_{IV_1}	A_{IV_2}
1.5	0, 0224820950	0, 0131975930	0, 0011965960	0, 0088818250
1.6	165599590	83735350	18380840	67037650
1.7	118309530	51614910	19070370	48910730
1.8	82095950	30859070	16850230	34446140
1.9	55364764	17881490	13516496	23410530
2.0	36290460	10039990	10107084	15360180
2.1	23113461	5462477	7137103	9737414
2.2	14294771	2880310	4791481	5969871
2.3	8576333	1472121	3068168	3543013
2.4	4985008	729369	1875605	2037513
2.5	2802382	350375	1093273	1136221
2.6	1519799	163181	605645	614950
2.7	792536	73695	316730	323183
2.8	395377	32240	154450	165013
2.9	187245	13715	68607	81890
3.0	83005	5626	26214	39544

TABLE III (continued)

First-order, threebody interactions, in units of βe^2 , for triangles of type 60° and 90° , plus twobody interactions (column B_V), as function of $x = \beta R$.

$x = \beta R$	A_V	A_{VI_1}	A_{VI_2}	B_V
1.5	-0, 0287558040	- 0, 0175745070	- 0, 0040422450	0, 1426265550
1.6	- 232692330	- 130562080	- 22874500	1125817370
1.7	- 185296380	- 95309750	- 10822950	881313850
1.8	- 145141330	- 68371090	- 3198270	683395980
1.9	- 111779950	- 48197199	- 1113490	524307590
2.0	- 84605350	- 33385682	- 3135180	397522210
2.1	- 62908076	- 22721096	- 3714345	297486670
2.2	- 45932137	- 15189639	- 3491254	219450370
2.3	- 32920826	- 9972769	- 2905517	159347740
2.4	- 23154258	- 6428324	- 2229073	113692550
2.5	- 15976594	- 4066965	- 1607440	79550260
2.6	- 10812951	- 2524670	- 1101694	54442850
2.7	- 7177223	- 1537214	- 722830	36318610
2.8	- 4672195	- 917782	- 456036	23500880
2.9	- 2982898	- 537140	- 277696	14641710
3.0	- 1867977	- 308098	- 163630	8676920

TABLE IV

Total first-order, threebody interactions, in units of βe^2 , for a central atom and twelve nearest neighbors, in the hcp- and fcc-lattices, and their difference, as function of $x = \beta R$.

$x = \beta R$	$(E_{a\Delta})_{hcp}$	$(E_{a\Delta})_{fcc}$	$(E_{a\Delta})_{hcp} - (E_{a\Delta})_{fcc}$
1.5	- 0, 539651706	- 0, 540863298	+ 0, 001211592
1.6	- 0, 400869702	- 0, 401180874	+ 0, 000311172
1.7	- 0, 304925268	- 0, 304578342	- 0, 000346926
1.8	- 0, 236365758	- 0, 235685310	- 0, 000680448
1.9	- 0, 185137335	- 0, 184377906	- 0, 000759429
2.0	- 0, 145154105	- 0, 144465280	- 0, 000688825
2.1	- 0, 112965875	- 0, 112411272	- 0, 000554603
2.2	- 0, 086706107	- 0, 086294046	- 0, 000412061
2.3	- 0, 065340859	- 0, 065052697	- 0, 000288162
2.4	- 0, 048203016	- 0, 048010743	- 0, 000192274
2.5	- 0, 034750956	- 0, 034627889	- 0, 000123067
2.6	- 0, 024459619	- 0, 024383613	- 0, 000076006
2.7	- 0, 016801321	- 0, 016756050	- 0, 000045272
2.8	- 0, 011263773	- 0, 011237515	- 0, 000026258
2.9	- 0, 007370886	- 0, 007356076	- 0, 000014809
3.0	- 0, 004710541	- 0, 004702504	- 0, 000008037

TABLE IV (continued)

Total pair-interactions, and relative first-order threebody interactions, in units of βe^2 , for a central atom and twelve nearest neighbors, in the hcp- and fcc-lattices, as function of $x = \beta R$.

$x = \beta R$	$(E_{a-b})_{\text{hcp or fcc}}$	$(E_{a\Delta})_{\text{hcp}}/E_{a-b}$	$(E_{a\Delta})_{\text{fcc}}/E_{a-b}$
1.5	0, 855759330	- 0, 630611536	- 0, 632027345
1.6	0, 675490422	- 0, 593449868	- 0, 593910529
1.7	0, 528788310	- 0, 576649033	- 0, 575992956
1.8	0, 410037588	- 0, 576449001	- 0, 574789523
1.9	0, 314584554	- 0, 588513748	- 0, 586099678
2.0	0, 238513326	- 0, 608578595	- 0, 605690601
2.1	0, 178492002	- 0, 632890402	- 0, 629783243
2.2	0, 131670222	- 0, 658509613	- 0, 655380122
2.3	0, 095606244	- 0, 683437156	- 0, 680423109
2.4	0, 068215530	- 0, 706628195	- 0, 703809572
2.5	0, 047730156	- 0, 728071297	- 0, 725492902
2.6	0, 032665710	- 0, 748785781	- 0, 746459011
2.7	0, 021791166	- 0, 771015272	- 0, 768937742
2.8	0, 014100528	- 0, 798819299	- 0, 796957071
2.9	0, 008785026	- 0, 839028378	- 0, 837342632
3.0	0, 005206152	- 0, 904802879	- 0, 903259186

IMPLICATIONS OF RESULTS FOR POSSIBLE FUTURE WORK

The evaluation of threebody interactions in first-order of perturbation theory being terminated, the next step consists in calculating the threebody-second-order (2-2) effect. This term is on one side more complicated in that second-order perturbation theory is used, but simpler in that we consider here the interaction between a diatomic unit and a single atom. Electron exchange between the atom and the pair is consistently neglected; taking it into account implies a higher-order correction in the present scheme.

The perturbation hamiltonian H'_{abc} takes a particularly simple form in this case. Namely, the second-order interaction between the two atoms which form the diatomic unit (ab) is not changed by the presence of the third atom (c), since (c) does not overlap with (ab). Consequently, for the evaluation of the threebody component, we may restrict ourselves to the part $H'_{(ab)c}$ of H'_{abc} , giving only the electrostatic interaction between the pair (ab) and the third atom (c). As a result, the interaction between atoms a and b does not occur, which simplifies the calculations considerably.

Further, the summation over all excited states of the three atoms will be carried out by replacing the resonance denominators by an average excitation energy, which leaves only matrix elements of $H'_{(ab)c}$ and $(H'_{(ab)c})^2$ for the unperturbed ground state. The value of this average excitation energy does not matter, since it drops out in a calculation of the relative deviation from the assumption of twobody interactions. The total number of resulting integrals is 64, mostly of three-center type with Gaussian integrands, except for factors $1/r_{ij}$ or $(1/r_{ij})(1/r_{kl})$, where i, j, k, l denote any one of the three electrons or the three nuclei, with $i \neq j$, $k \neq l$. These integrals are in part direct, in part of exchange type; the exchange involves electrons of the pair (ab), but

not of atom c. Further stages of the research project, such as the calculation of elastic constants (deviations from the Cauchy-relations) will then be devised along similar lines, pending the outcome of the present computation.

PUBLICATIONS AND CONFERENCES

Three Special Technical and Scientific Reports were issued during the first year of the Contract. A manuscript entitled "Systematic Analysis of Manybody Interactions in Molecular Crystals" was submitted for publication in The Physical Review (August 1961).

Colloquium talks on this research were delivered by the principal investigator at Ohio State University, Columbus, Ohio (November, 1960), at the Max-Planck Institut für Physik und Astrophysik, Munich (June, 1961) and at the National Bureau of Standards, Washington D.C. (October, 1961). In addition, the research was discussed at several colloquia of the Battelle-Geneva Institute.

PERSONNEL ON THE CONTRACT

The following persons were employed part-time under the contract during the past year :

- 1) Dr Laurens Jansen, principal investigator;
- 2) Dr Barbara Kohin, visiting scientist, the Catholic University of America, Washington D.C., as off May 1961;

- 3) Mr François Siegrist, mathematics student, Federal Institute of Technology, Zurich, Switzerland, during August 1961;
- 4) Mr Maurice Marchais, Mr. Raymond Lenoir, Mrs Jolan Targonski, scientific personnel associated with the digital computer Bull Gamma AET.

No changes in research policies by the Contractor have occurred during the period October 1, 1960 - September 30, 1961.

SUMMARY OF NUMBER OF MANHOURS ON CONTRACT

The total numbers of manhours expended on the contract for the individuals mentioned in the previous section are :

- Dr Laurens Jansen	: 1 000 hrs
- Dr Barbara Kohin	: 100 hrs
- Mr. François Siegrist	: 150 hrs
- Mr. Raymond Lenoir	: 125 hrs
- Mr. Maurice Marchais	: 250 hrs
- Mrs Jolan Targonski	: 300 hrs

Not listed are hours expended for secretarial services, preparation and processing of Technical Reports and similar items.

No important property was acquired during the contract period at direct contract expense.

Geneva, November 15, 1961
LJ/gbs - Z-9219

Fig. 1

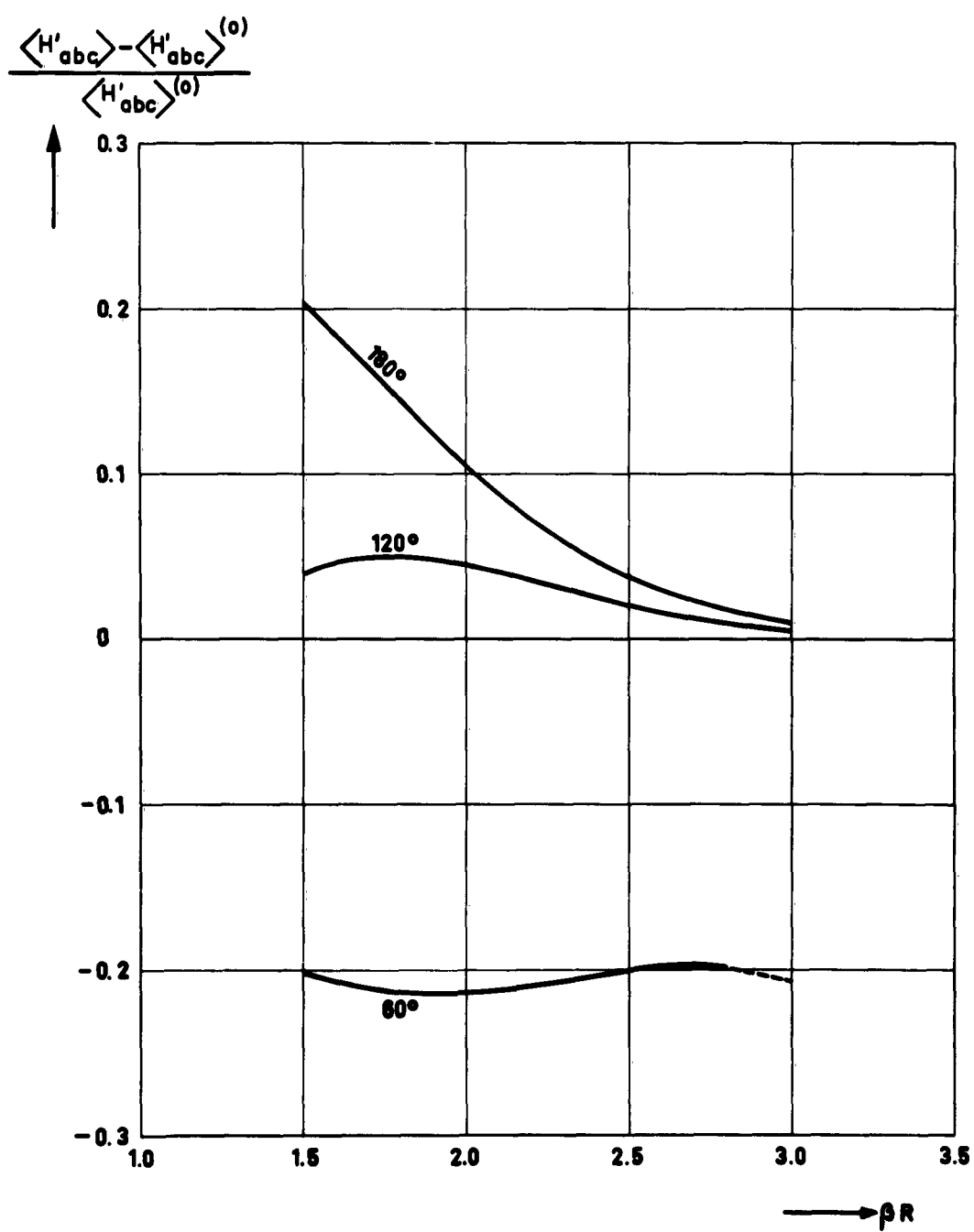


Fig. 2

